DEGRADATION STUDY FOR DISLODGEABLE DIAZINON RESIDUE ON HEAD LETTUCE AND CHINESE CABBAGE FOLIAGE IN MONTEREY AND SANTA CRUZ COUNTIES

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SUMMARY

Six fields (5 head lettuce and 1 Chinese cabbage) were sampled for dislodgeable foliar pesticide residue after an application of Diazinon. Samples were collected before the application, immediately post, and periodically for three to four days post-application. Current California regulation does not allow reentry to this crop until the spray is dry (not to exceed 24 hours). A safe level for Diazinon has been calculated to be 4.00 ug/cm^2 (4). In all five lettuce fields, mean residue levels were never above this level. Therefore, it appears that for all fields sampled the current reentry interval would be adequate.

INTRODUCTION

In June 1971, the California Department of Food and Agriculture established reentry intervals for specific crop/pesticide combinations (California, 1985). A reentry interval is the time period that must elapse between the application of a pesticide and the entry of unprotected workers into the treated area. This waiting period was instituted to allow sufficient time for toxic materials to environmentally degrade to a low-toxicity residue level. The adequacy of these safety intervals has not been completely evaluated since their introduction. This study was initiated to validate the existing reentry interval. The objective of this study was to monitor the foliar decay rate of Diazinon. This study is one of several studies conducted for the purpose of validating reentry intervals.

Diazinon is a Toxicity Category II or III pesticide (depending on formulation type and percent active ingredient) organophosphate insecticide used extensively in agriculture on various vegetable and fruit crops in California. Diazinon has an oral LD_{50} (rat) of 76 mg/kg and an acute dermal LD_{50} (rat) of 455 mg/kg (NIOSH, 1979). A common result of organophosphate poisoning is cholinesterase inhibition.

This study shows the rate at which the residue levels decline to safe levels.

METHODS AND MATERIALS

With the assistance of both the Monterey and Santa Cruz County Agricultural Commissioner's (CAC) offices, cooperation was obtained from growers and pest control operators (PCOs) who would be using Diazinon. The material used on all the head lettuce fields was Diazinon Ag 500 (Clean Crop), EPA Reg. No. 34704-41, registered by Platte Chemical Company. The material contains 48 percent active ingredient (4 pounds Diazinon per gallon) with a maximum application rate of one pint per acre. The application rate for all the head lettuce fields studied was one pint of the formulated product per acre, with a dilution rate of 100 gallons of water per acre. Diazinon 50W, EPA Reg. No. 100-460, registered by Ciba-Geigy, was used on the Chinese cabbage field. This material consists of 50 percent active ingredient with a maximum rate of one pound of the formulated product per acre. The application rate on the Chinese cabbage field was three-quarter's of a pound per acre. The dilution rate was 60 gallons of water per acre.

The reentry interval for all the fields studied was 48 hours (because of other materials applied with the Diazinon). All applications were delivered by ground equipment (boom). The tank mix for all the head lettuce fields also contained Phosdrin 4E, Pounce, Manzeb, and Micro Spreader-Sticker. The tank mix for the Chinese cabbage field also contained Phosdrin 4E, Methomyl, and Manzate.

The selected block in each field was divided into three areas. Non-adjacent rows from each of these areas were chosen as the sampled rows. These rows were designated as A, B, and C. Samples consisted of composites from each of the rows. Each sampled row was marked at the beginning of the row and at the locations of the first plant and last plant sampled in that row. In Row A, sampling began on the plant 25 meters from the edge of the field. In Row

B, sampling started near the middle of the row; and in Row C, sampling began such that the turn-around point on that sampling row was 25 meters from the opposite end. This layout approximated a diagonal across the sampled block. Sixteen (16) leaf punches were taken from each row; 8 on the right, and 8 on the left of each row. Punches were taken from leaves presenting the greatest exposed surface area. Replicate samples were obtained simultaneously from sites spaced as close together as possible.

Pre-application samples were collected prior to the application. Samples were also taken immediately after the application and continued throughout three to four days post-application.

Samples were taken using a 2.54 cm diameter leaf punch. Each sample contained 48 leaf discs accumulated in a four ounce glass jar. The leaf punch was cleaned with alcohol between row sampling. Sample jars were sealed with aluminum foil, capped, and stored on wet ice. The ice was constantly replenished to insure temperature stability. All required protective equipment was worn by the personnel while sampling.

Samples were delivered to the mobile chemistry laboratory stationed at the Monterey CAC's office for analysis. The procedure for gas chromatography (GC) analysis of organophosphates (OPs) is given in Appendix I. The minimal detectable level for Diazinon is 0.002 ug/cm^2. Weather conditions during the study varied.

RESULTS

The analytical results for Diazinon residue analyses are given in Table 1. The dislodgeable residue decay rates are illustrated in Figures 1, 2 and 3. Levels found indicate a rapid decay of the material. Knaak, et. al. (1980) has calculated "safe levels" of dislodgeable residue for certain pesticides. This is a level of foliar residue in which an unprotected field worker could reenter a treated area with little or no hazard. A safe level has not been established for Diazinon. However, by comparing dermal LD_{50} values with chemicals that do have calculated safe levels, a safe level can be estimated for Diazinon. This level has been estimated at 4.00 ug/cm^2 (Maddy, 1985). Average residue levels never were above 4.00 ug/cm^2 in any sample collected after application. Figure 1 is for fields 1 and 2, as they were sprayed on the same dates and by the same PCO. Figure 2 contains the curves for field 3 and 4, Figure 3 has curves for fields 5 and 6 for similar reasons, stated for fields 1 and 2.

DISCUSSION

Under the conditions in which this study was conducted, the residue levels dropped very rapidly and should not pose a health risk to field workers. Since this study's conditions reflect actual agricultural practices in this area, this data would support the current reentry interval. There appears to be no need to increase this reentry interval according to the data generated in this study. Further study may be of interest to determine the reasons for the variation in sample results.

TABLE 1

Dislodgeable Degradation of Foliar Residues of Diazinon (ug/cm^2)

FIELD # 1 - Head Lettuce

DAY	REP A	REP B	MEAN
Pre-Application	N.D.	N.D.	N.D.
6 Hours	0.433	0.300	0.367
9 Hours	0.444	0.227	0.336
12 Hours	0.219	0.140	0.180
18 Hours	0.051	0.057	0.054
30 Hours	0.058	0.049	0.054
36 Hours	0.054	0.043	0.049
42 Hours	0.034	0.032	0.033
54 Hours	0.030	0.030	0.030
60 Hours	0.011	0.021	0.016
66 Hours	0.016	0.016	0.016
78 Hours	0.025	0.012	0.019

FIELD # 2 - Head Lettuce

DAY	REP A	REP B	MEAN
Pre-Application	N.D.	N.D.	N.D.
6 Hours	0.439	0.252	0.346
9 Hours	0.286	0.155	0.220
12 Hours	0.121	0.126	0.124
18 Hours	0.014	0.049	0.032
30 Hours	0.067	0.089	0.078
36 Hours	0.064	0.053	0.058
42 Hours	0.009	0.007	0.008
54 Hours	0.015	0.026	0.020
60 Hours	0.056	0.035	0.041
66 Hours	0.046	0.046	0.046
78 Hours	0.025	0.025	0.025

FIELD # 3 - Head Lettuce

DAY	REP A	REP B	MEAN
Pre-Application	N.D.	N.D.	N.D.
1 Hour	0.170	0.185	0.178
12 Hours	0.017	0.046	0.032
18 Hours	0.015	0.019	0.017
24 Hours	0.009	0.005	0.007
36 Hours	0.010	0.011	0.011
42 Hours	0.006	0.005	0.006
48 Hours	0.007	0.007	0.007
60 Hours	0.005	0.006	0.006

FIELD # 4 - Head Lettuce

DAY	REP A	REP B	MEAN
Pre-Application	N.D.	N.D.	N.D.
1 Hour	0.165	0.152	0.158
12 Hours	0.062	0.049	0.056
18 Hours	0.018	0.014	0.016
24 Hours	0.010	0.009	0.010
36 Hours	0.009	0.002	0.006
42 Hours	0.006	0.006	0.006
48 Hours	0.005	0.005	0.005
60 Hours	0.004	0.004	0.004

FIELD # 5 - Head Lettuce

DAY	RE A	REP B	MEAN
Pre-Application	N.D.	N.D.	N.D.
1 Hour	0.202	0.170	0.186
6 Hours	0.217	0.082	0.150
14 Hours	0.089	0.169	0.129
24 Hours	0.038	0.021	0.030
36 Hours	0.030	0.029	0.030
48 Hours	0.016	0.023	0.020

FIELD # 6 - Chinese cabbage

DAY	REP A	REP B	MEAN
Pre-Application	N.S.	N.S.	N.S.
1 Hour	N.S.	0.221	0.221
6 Hours	0.244	0.115	0.180
14 Hours	0.070	0.075	0.072
24 Hours	0.012	0.053	0.032
36 Hours	0.058	0.042	0.050
48 Hours	0.022	0.007	0.014

MDL = 0.002 ug/cm^2
N.D. = None detected
N.S. = Not sampled

FIGURE 1: Dislodgeable foliar residues of diazinon on head lettuce (Fields 1 & 2).

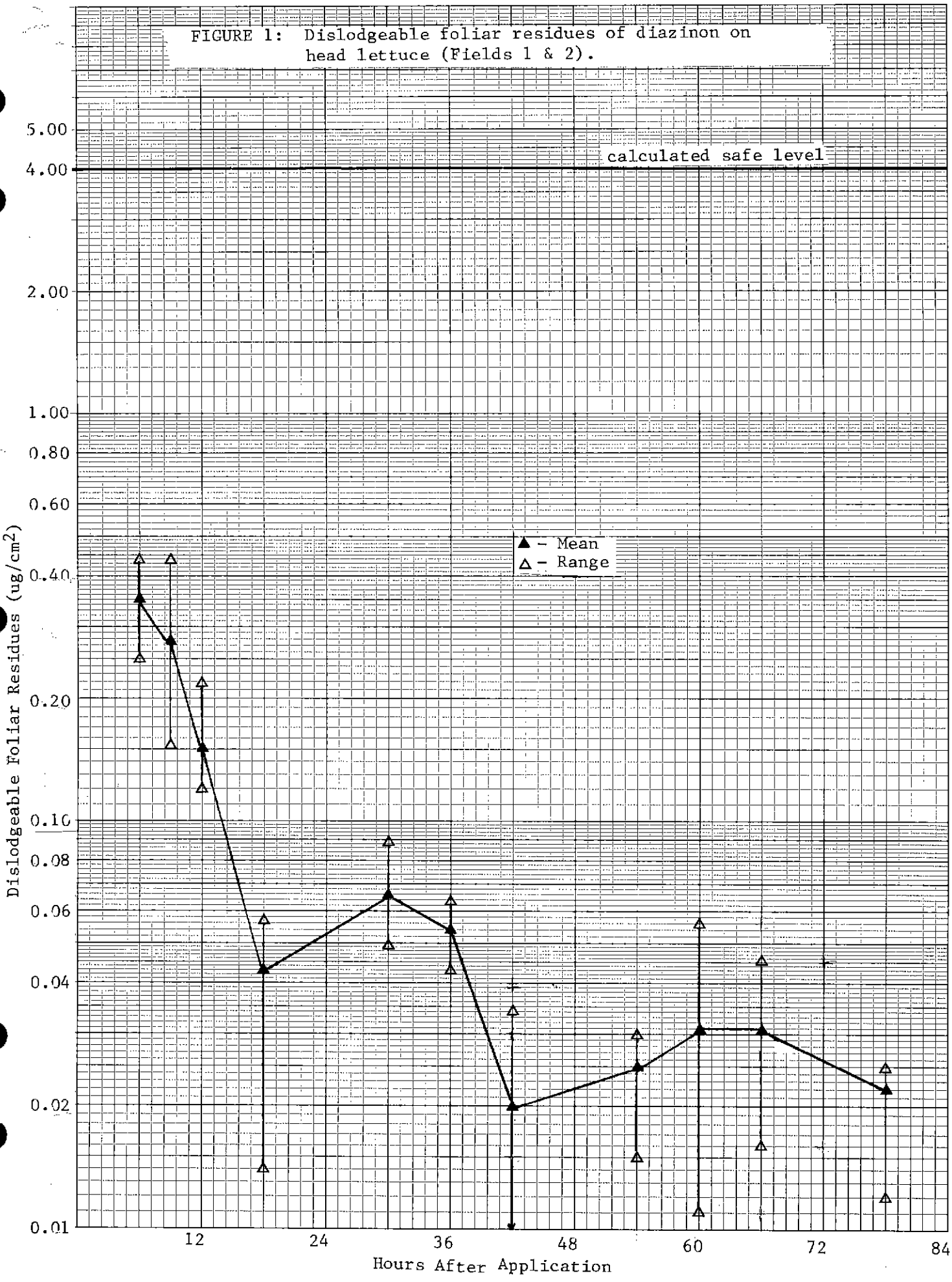


Figure 2: Dislodgeable foliar residues of Diazinon on head lettuce (Fields 3 & 4).

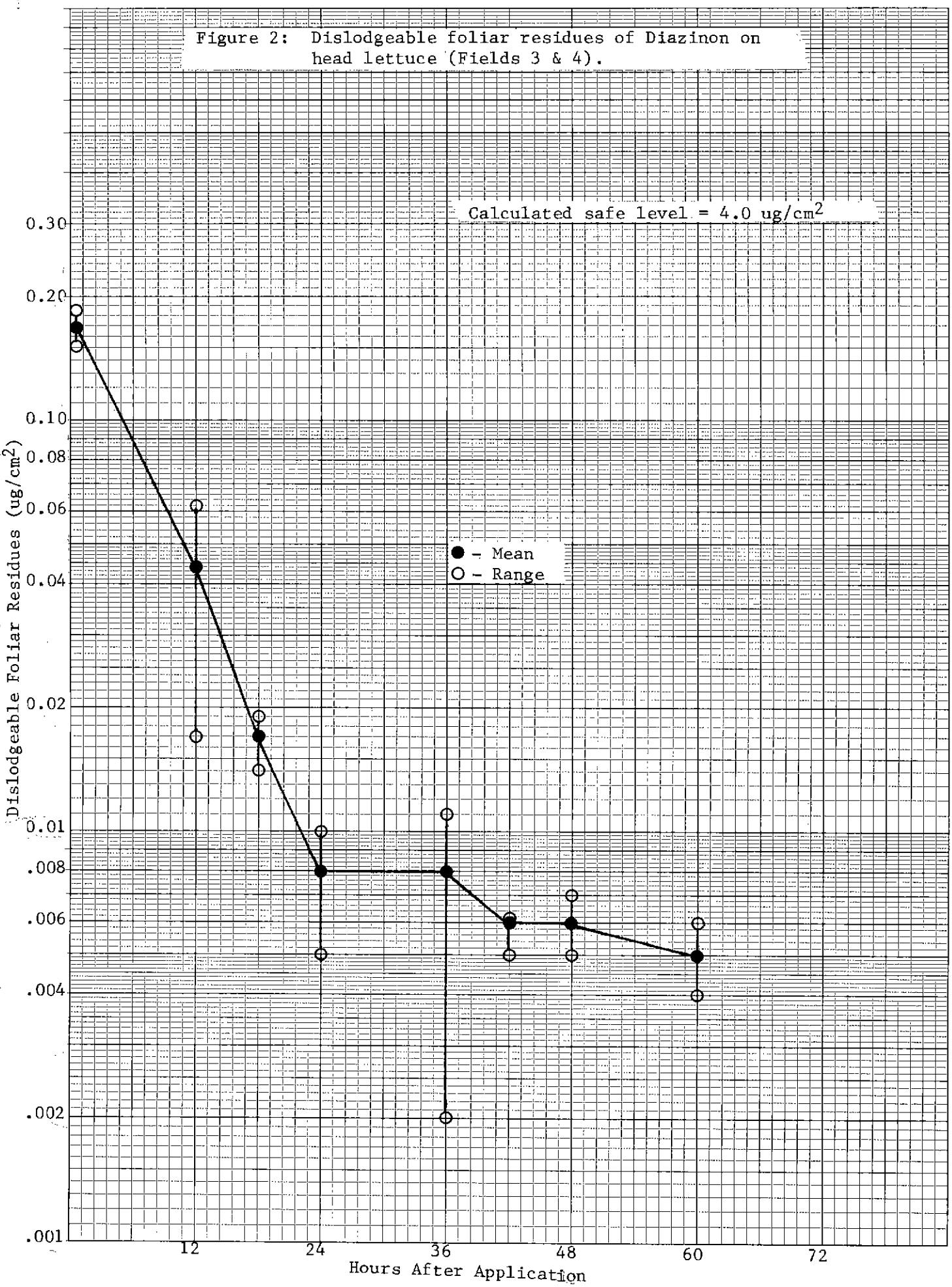
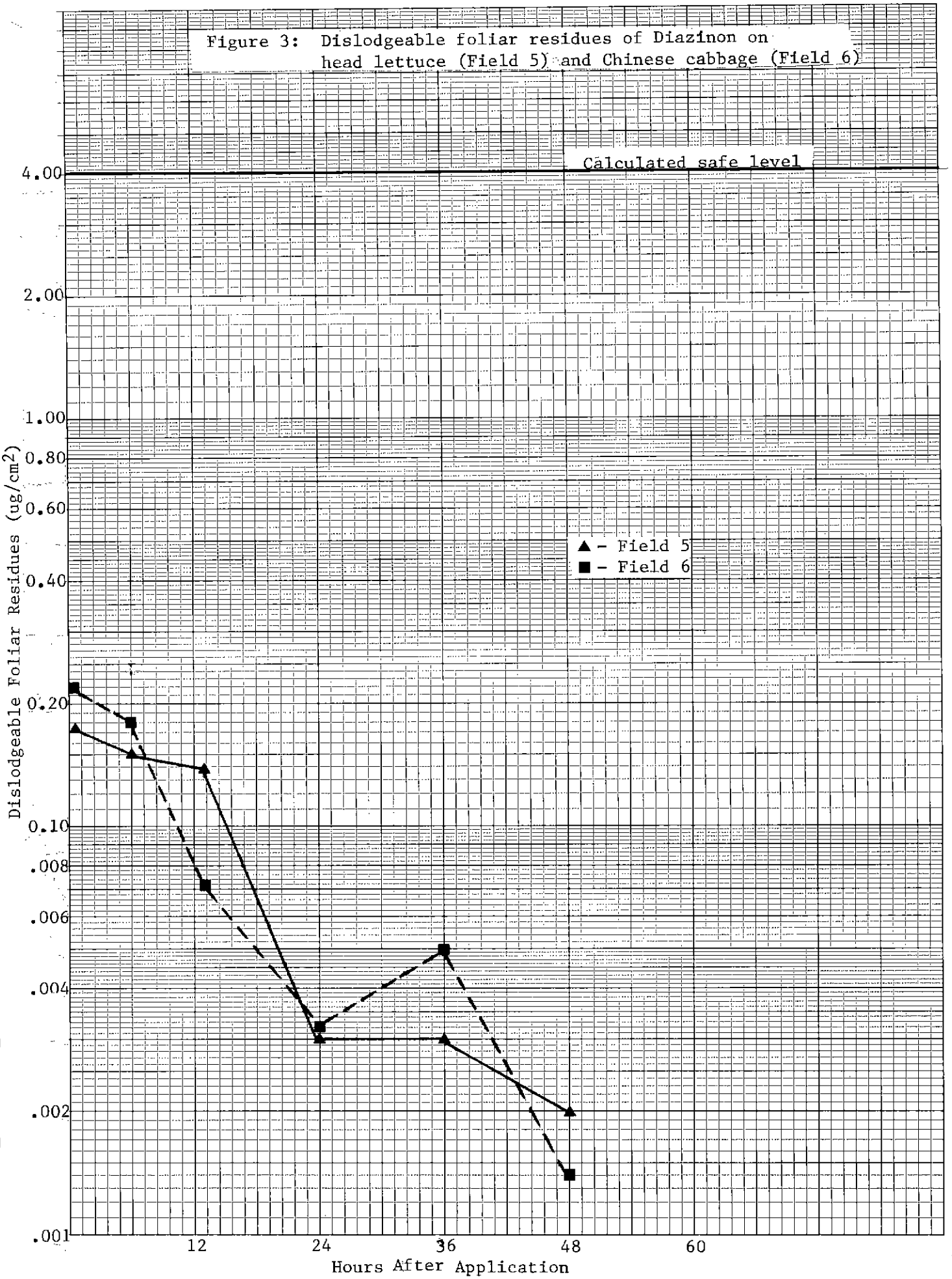


Figure 3: Dislodgeable foliar residues of Diazinon on head lettuce (Field 5) and Chinese cabbage (Field 6)



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APPENDIX I

ANALYTICAL PROCEDURE FOR THE SCREENING OF ORGANOPHOSPHATE DISLODGEABLE PESTICIDE RESIDUES

SCOPE: This method covers the extraction of all of the common organophosphate pesticides from the surfaces of leaves or foliage.

PRINCIPLE: The organophosphate pesticide is washed off of the leaf surface by rotating the sample with water containing a small amount of surfactant. The aqueous washings are then extracted with an organic solvent. The solvent is concentrated or diluted as needed and the organophosphate determined by suitable gas or liquid chromatography.

REAGENTS AND EQUIPMENT:

1. Sample rotator capable of holding the sample jars and rotating them at about 30 rpm.

2. Separatory funnel, 250 or 500 ml size.

3. Funnel, 60 degree and about 3 inch diameter.

4. Beakers, 400 ml and 150 ml sizes.

5. Hot plate with waterbath and blow-down device or rotary evaporator.

6. Suitable gas chromatograph or liquid chromatograph for chemical to be assayed. (Typically GC with NPD detector.)

7. Glass wool, solvent washed.

8. Sodium Sulphate, anhydrous, granular. Test for interferences.

9. Ethyl Acetate, nanograde. Pre saturate the ethyl acetate by shaking with water prior to use. Test for interferences. Other solvents may be needed in specific cases or if specific classes of pesticides are to be extracted concurrently (i.e. methylene chloride for lannate or metasystox.)

10. Sur-Ten surfactant, 1:50 solution in distilled water.

ANALYSIS:

1. Add 50 ml of water plus 4 drops of Sur-Ten solution to the leaf punches in the original sample jar. Take care not to loose the foil jar lid liner or any dirt or material from the liner or jar. If foil is torn or does not cover the entire lid you may wish to add a second layer of clean foil on top of the original foil liner.

2. Rotate the sample jar for 20 minutes at about 30 rpm. Observe if there is agitation of the leaf punches and water. More water may be required or the inspectors may have to reduce the number of leaf punches per jar if agitation is insufficient.

3. Decant the aqueous solution into the separatory funnel. Repeat steps 1 and 2 above two more times, combining the washings in the separatory funnel.

4. Add 50 ml of water saturated ethyl acetate to the separatory funnel and agitate gently for about two minutes, taking care not to emulsify the solvent. Allow the water and solvent to separate. Drain the aqueous (bottom) layer into the 400 ml beaker and retain.

5. Slowly drain the ethyl acetate layer through about 15 to 20 grams of sodium sulphate in the 60 degree funnel into the 150 ml beaker. Use glass wool to plug the funnel opening.

6. Repeat steps 4 and 5 twice more using 25 to 30 ml of ethyl acetate. Combine the extracts in the 150 ml beaker.

7. Concentrate (or dilute) the combined extracts to an appropriate level for gas or liquid chromatography. During concentration steps take care not to go to dryness as some of the organophosphates may be lost.

CALCULATIONS: Calculate results in micrograms or nanograms per square centimeter of leaf surface area (account for both sides of leaf).

Total Area = 2 * N * 3.142 * R * R

Where N = number of punches
R = radius of punch in cm

$$\text{ug/sq. cm} = \frac{(\text{pk ht or area - smp}) * (\text{ng std inj.}) * (\text{ml final vol.})}{(\text{pk ht or area - std}) * (\text{ul inj.}) * (\text{Tot. Area})}$$

DISCUSSION: As was noted in the Reagents section there may be some cases where a different solvent may be required due to the particular OP being extracted or due to a combination of pesticides which are to be concurrently extracted.

The older scheme of rotating samples for 1 hour, then 30 minutes, and finally with a 10 second wash with plain water appears to yield the same washing efficiency.

Instrument conditions may vary widely with the different OP's being looked for and what instrumentation is available. Typically a gas chromatograph equipped with an NPD (or alternatively an FPD in P mode) is employed with non-polar column such as SP-2100 or OV-101.

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